# SUBJECT INDEX


A

Acetone
  gas phase basicity of, 196–97
Acetylene-hydrogen chloride dimer
  rotational spectra of, 288–92
Acid-base chemistry
  see Gas phase acid-base chemistry
Acids
  proton tranfer reactions and, 205
Adatom-adatom interaction energies
  order-disorder phase transitions and, 226–28
Adenine
  polarized transitions of, 338–39
Alanine
  proton affinity of, 196
Alkenes
  proton transfer reactions and, 206
Allene
  vibration-rotation spectroscopy and, 264
Amino acids
  gas phase acidities of, 190–91
  gas phase basicities of, 195–96
Ammonia
  proton affinity of, 195
Analytically integrated Magnus method
  kinetic sensitivity analysis and, 425–26
Anthracene-dimethylaniline
  fluorescence spectra of, 146
Aqueous solutions
  structural properties of, 156–73
Argon
  proton transfer reactions and, 206
Aromatic hydrocarbons
  gas phase basicities of, 196
Asymmetric rotors
  vibration-rotation spectroscopy and, 266–67
Atomic iodine laser, 575–76

B

Benzene
  internal conversion radiationless transition in, 148
Benzyne
  proton affinity of, 195
Biacetyl
  polyatomic quantum beats of, 135
Boundary layer theory
  development of, 23–24

C

Carbon disulfide
  vibration-rotation spectroscopy and, 261
Carbon monosulfide
  vibration-rotation spectroscopy and, 260
Carbon monoxide lasers, 569–72
Carbon suboxide
  vibration-rotation spectroscopy and, 263
Carbonyl compounds
  gas phase basicities of, 196–97
Chemical ionization mass spectrometry
  gas phase acid-base chemistry and, 189
Chemical lasers, 557–86
  initiation of
    methods of, 562–65
  kinetic modeling of, 582–86
  lasing action of
    requirements for, 559–61
  types of, 565–82
Chemical reactions
  chemical laser initiation and, 564
Chemical vapor deposition
  thermochemical deposition and, 91
Chemisorbed overlayers
  order-disorder phase transitions in, 217–42
Combustor products
  chemical laser initiation and, 564–65
Cubane
  vibration-rotation spectroscopy and, 268

Cycloalkanes
  pseudorotation and, 308
Cyclobutane
  pseudorotation and, 310
Cyclopentane
  pseudorotation and, 302–5
Cytosine
  polarized transitions of, 343–44

D

Density functional theory, 631–51
  exact formulations of, 632–37
  local approximations of, 638–42
  wave function theory and, 646–48
Diatomic molecules
  N-electron
    rotational coordinates of, 10–11
  vibration-rotation spectroscopy and, 259–60
Dielectric fluids
  behavior of electrons in, 465–68
Dielectric phenomena
  electrical conductivity and, 122–23
Dienes
  proton transfer reactions and, 206
Diffusion coefficients
  diffusion-controlled reactions and, 497–501
Diffusion-controlled reactions, 493–521
  concentration dependence of, 496–505
  Fokker-Planck equation and, 511–14
  gated, 517–19
  ionic, 519–20
  mean first passage times and, 514–16
  mutual diffusion coefficient and, 497–99
  self-diffusion coefficient and, 499–501
  simulation of, 516–17

Dimers
  weakly bound
    rotational spectra of, 287–98
Dimer spectroscopy
  pulsed-nozzle, 275–99
1,1-Dimethylsilaethylene
  proton affinity of, 195
Dinucleosides
  room temperature fluorescence of, 351–52
Dioxalane
  pseudorotation and, 312
Dipole moments
  of formaldehyde, 51–52
  of thioformaldehyde, 51–52
DNA
  room temperature fluorescence of, 352–53
DNA bases
  room temperature fluorescence of, 348–53

E

Edwards theory of elasticity, 376–80
Eichinger theory of elasticity, 380–82
Elasticity, 359–83
  Edwards theory of, 376–80
  Eichinger theory of, 380–82
  Flory constrained junction theory of, 373–76
  James-Guth theory of, 369–71
  thermodynamics and mechanics of, 360–63
  Wall-Flory theory of, 371–73
Electrical conductivity
  dielectric phenomena and, 122–23
Electrical discharge
  chemical laser initiation and, 563
Electron beams
  chemical laser initiation and, 563–64
Electron-device fabrication
  laser microchemistry and, 77–99
Electronic transition lasers, 575–82
Electrons
  behavior in dielectric fluids, 465–68
Enamines
  proton affinity of, 195
Energy transfer lasers, 573–74
Entropy
  elastic restoring force and, 360–61
  molecular dynamics and, 104–5
Equilibrium
  fluids at
    molecular dynamics of, 106–7
  fluids close to
    molecular dynamics of, 107–9
  fluids far from
    molecular dynamics of, 109–10
Esters
  proton transfer reactions and, 205
Ethane
  proton transfer reactions and, 205
Ethylene
  vibration-rotation spectroscopy and, 266
Ethylideneimine
  proton affinity of, 195
Excimer fluorescence
  polarization of, 345–46
Excited state constants
  vibration-rotation spectroscopy and, 257–59
Excited state dynamics, 129–50
  dispersed fluorescence and, 136–40
  intersystem crossing and, 147–48
  vibrational randomization and, 131–36
Exothermic reactions
  activation energy for, 15

F

Fabry-Perot cavity, 280–81
Flames
  chemical laser initiation and, 564
Flash photolysis
  chemical laser initiation and, 562–63
Flory constrained junction theory of elasticity, 373–76
Flowing afterglow
  gas phase acid-base chemistry and, 188–89
Fluid shockwaves, 121
Fluorine
  gas phase acidities and, 191
  gas phase basicities and, 196–97
*p*-Fluorotoluene
  IVR decay time in, 141
Fokker-Planck equation
  diffusion-controlled reactions and, 511–14
Formaldehyde
  Coriolis and Fermi interactions of, 34–37
  dipole moments of, 51–52
  ground state rotational constants of, 33–34
  higher excited states of, 47–51
  molecular structure of, 32, 37–39, 45–46
  perturbations of, 44–45
  rotational structure of, 41, 46–47
  singlet-triplet interactions of, 53–54
  spectroscopy of, 31–56
  vibration-rotation spectroscopy and, 266–67
  vibrational frequencies of, 32, 41–44, 47–48
  vibronic structure of, 39–40, 46
Formaldehyde photochemistry, 525–53
  collision free $S_1$ lifetimes and, 530–36
  collisions and, 536–40
  decay mechanism in, 544–50
  energy states, potential surfaces, and dissociation limits and, 526–28
  products of, 540–44
Fourier amplitude sensitivity test
  kinetic sensitivity analysis and, 429–31
Fourier transform spectroscopy, 248–50
Fuel spray burning
  nonhomogeneous kinetics and, 476–80

G

Gas phase acid-base chemistry, 187–212
  experimental methods in, 187–89
  gas phase/solution transition in, 211–12
  kinetics of, 204–10
  thermodynamics of, 189–204
Gas phase acidity
  thermodynamic properties of, 189–93
Gas phase basicity
  thermodynamic properties of, 193–204
Glycine
  gas phase acidity of, 190–91
  proton affinity of, 196
Granular materials
  flow of, 121–22
Green's function method
  kinetic sensitivity analysis and, 423–25

Ground state constants
vibration-rotation spectroscopy and, 256–57
Guanine
polarized transitions of, 336–37

H

Halide ions
proton transfer reactions and, 205
Hamiltonians, 61–69
applications of, 69–73
HBJ, 64–65
nonrigid bender, 66–68
rigid bender, 65–66
semirigid bender, 68–69
Harmonic oscillators, 63–69
Heat capacity
of supercooled water, 607
Heat conductivity
viscosity and, 120–21
High pressure mass spectrometry
gas phase acid-base chemistry and, 188
Hilbert paradox, 23
Hirschfelder's rule, 14–15
Hydrogen
interaction with palladium, 230–42
interaction with surface of nickel, 223–29
molecular
coulombic energy/total binding energy ratio of, 14
polarization of, 7–9
potential energy surface of hydrogen atom approaching, 15–16
proton transfer reactions and, 206
Hydrogen halide lasers, 565–69
Hylleraas variational principle
polarization of molecular hydrogen and, 8

I

Infrared laser spectroscopy, 250–53
Insulator films
thermochemical deposition and, 91–92
Intersystem crossing
internal conversion and, 147–48
Iodine heptafluoride
pseudorotation and, 323
Ion cyclotron resonance spectrometry
gas phase acid-base chemistry and, 188
Ionic solutions
anion-water correlation functions in, 169–71
cation-water correlation functions in, 163–69
ion-ion correlation functions in, 171–73
ion-water coordination in, 160–63
neutron quasi-elastic spectroscopy and, 173–84
neutron scattering from, 155–84
Ionic systems
diffusion-controlled reactions in, 503–4
Ising model
interaction of hydrogen with palladium and, 232–34
Isocyanate
linear equilibrium structure of, 71

J

James-Guth theory of elasticity, 369–71

K

Kinetic sensitivity analysis, 419–60
derived sensitivities and, 439–42
functional, 451–59
derived sensitivity densities and, 457–59
elementary sensitivity densities and, 451–56
laboratory data analysis and, 442–48
space-time, 434–39
temporal, 421–34
global methods of, 428–31
local methods of, 421–28
stochastic systems of, 431–34
structural elements in, 448–51

L

Laser etching, 81–86
mechanisms of, 83–86
technique of, 81–83
Laser microchemistry, 77–99
applications of, 97–98
etching and, 81–86
liquid photochemistry and, 95–97
material deposition and, 86–94
photochemical dopant incorporation and, 96–97
Lasers
see specific type
Lattice gas model
interaction of hydrogen with palladium and, 232–35
Lennard-Jones particles
dielectric constant for, 123
Leucine
proton affinity of, 196
Linear molecules
vibration-rotation spectroscopy and, 261–63
Liquid photochemistry
laser microchemisty and, 95–96
Low-energy electron diffraction
order-disorder phase transitions and, 217–42

M

Magnetic circular dichroism
nucleic acid excited states and, 334
Magnetic field effects, 389–415
high field, 397–400
high field anisotropic yield and, 408–10
high field isotropic yield and, 407–8
isotropic and anisotropic, 403–5
low field, 400–1
low field isotropic yield and, 410–12
photosynthetic reaction centers and, 393–95
spin Hamiltonian and, 395–97
stochastic Liouville equation and, 396
Mass spectrometry
see specific type
Metal films
thermochemical deposition and, 91–92
Methane
vibration-rotation spectroscopy and, 267
Methinophosphide
vibration-rotation spectroscopy and, 261
Methyl fluoride
vibration-rotation spectroscopy and, 265–66
Methyl glyoxal
polyatomic quantum beats of, 135

Methyl halides
vibration-rotation spectroscopy and, 262
Molecular dynamics, 103–25
equilibrium
development of, 111–16
fluid phenomena and, 116–23
of fluids at equilibrium, 106–7
of fluids close to equilibrium, 107–9
of fluids far from equilibrium, 109–10
solid phenomena and, 123–24
Monomers
room temperature fluorescence of, 348–51
Monte Carlo simulations
order-disorder phase transitions and, 218
Muonium
nonhomogeneous kinetics and, 473–74
Mutual diffusion coefficient
diffusion-controlled reactions and, 497–99

N

Neutron quasi-elastic spectroscopy, 173–84
experimental results of, 178–81
neutron scattering and, 175–78
principles of, 174–75
Neutron scattering
from ionic solutions, 155–84
neutron quasi-elastic spectroscopy and, 175–78
Nickel
interaction of hydrogen with, 223–29
Nonhomogeneous kinetics, 470–89
deterministic, 475–80
models of, 474–89
stochastic, 480–89
Nuclear hyperfine coupling
weakly bound dimers and, 293–97
Nuclear magnetic resonance
ring conformation and, 313–14
supercooled water and, 611–14
Nucleation
supercooling and, 595–97
Nucleic acids, 329–55
luminescence of, 345–53
singlet excited states of, 331–45

O

Open-shell molecules
pseudorotation and, 324–25
Order-disorder phase transitions, 217–42
Organic radicals
gas phase acidities of, 191
Organometallic compounds
gas phase acidities of, 191
gas phase basicities of, 195

P

Palladium
interaction of hydrogen with, 230–42
Pentacene
fluorescence quantum yields and lifetimes in, 148
Phase metastability
equations of motion and, 112–13
Phenylalanine
proton affinity of, 196
Phosphorus pentafluoride
pseudorotation and, 302–5
Photochemical deposition, 86–91
Photoionization mass spectrometry
gas phase acid-base chemistry and, 189
Photoion-photoelectron coincidence
gas phase acid-base chemistry and, 189
Photosynthesis
photochemistry of, 391–93
Photosynthetic reaction centers
magnetic field effects in, 393–95
Phthalocyanine
collision-free vibrational randomization in, 140–41
Plane couette flow
simulation of, 108, 116–20
Polyatomic materials
flow of, 121–22
Polymeric materials
flow of, 121–22
Polynucleotides
room temperature fluorescence of, 351–52
Postitronium
nonhomogeneous kinetics and, 473–74
Potential energy surfaces
calculation of, 12–17
Proline
proton affinity of, 196
Proton affinities
gas phase, 193–97
Proton transfer reactions
kinetic properties of, 204–10
thermodynamic properties of, 189–204
Pseudorotation, 301–25
cyclopentane and, 302–5
molecules with central atom and, 321–23
open-shell molecules and, 324–25
phosphorus pentafluoride and, 302–5
ring molecules and, 308–21
Pulsed-nozzle, Fourier transform microwave spectrometer, 276–87
elements of, 278–83
operation of, 277–78
sensitivity and resolution of, 285–87
Purines
gas phase basicities of, 196
polarized transitions of, 334–36
singlet excited states of, 332–34
Pyrazine
intersystem crossing and, 147–48
Pyridines
proton transfer reactions and, 206
Pyrimidines
gas phase basicities of, 196
intersystem crossing and, 147–48
singlet excited states of, 332

Q

Quantum yield anisotropy, 395
Quasilinear molecules, 59–74
Quenching
formaldehyde photochemistry and, 538–40

R

Radiationless transitions
rotational effects and, 148
Raman spectroscopy
new developments in, 254–56
Rare gas excimer lasers, 576–77
Rare gas halide lasers, 577–80
Rayleigh-Schrödinger perturbation
polarization of molecular hydrogen and, 7–8
Reaction rates
absolute
theory of, 17–24
solvent effects on, 468–69

Renormalization group theory
order-disorder phase transitions and, 218–19, 229–29
Rhenium heptafluoride
pseudorotation and, 323
Rigid rotor harmonic oscillator, 62
Ring molecules
pseudorotation and, 308–21
Rotational coordinates
separation from N-particle Schrödinger equation, 9–12
Rotational relaxation
formaldehyde photochemistry and, 536–37
Rotational transition lasers, 574–75

S

Schrödinger equation
N-particle
separation of rotational coordinates from, 9–12
Selected ion flow tube
gas phase acid-base chemistry and, 188–89
Self-diffusion coefficient
diffusion-controlled reactions and, 499–501
Semiconductor films
thermochemical deposition and, 91–92
Semiconductors
liquid photochemistry and, 95–96
Shock heating
chemical laser initiation and, 564
Singlet-triplet interactions
of formaldehyde, 53–54
of thioformaldehyde, 54–56
Solid shockwaves
quantification of, 123–24
Solutions
see specific type
Solvated ions
acid-base reactions of, 211
Solvents
chemical reaction rates and, 468–69
Spectroscopy
of formaldehyde, 31–56
of thioformaldehyde, 31–56
see also specific type
Spherical rotors
vibration-rotation spectroscopy and, 267–68
Stark effect
dimer electric dipole moments and, 298
Stiff equations, 22–24
Sulfones
gas phase acidities of, 190
Sulfoxides
gas phase acidities of, 190
Supercooled water, 593–627
sampling techniques and, 601
simulations and theoretical interpretations and, 619–27
structural characteristics of, 601–4
thermodynamic properties of, 604–9
transport and relaxation properties of, 601–19
Supercooling
normal limit of, 593–600
Symmetric rotors
vibration-rotation spectroscopy and, 263–66

T

Tetracene
fluorescence quantum yields and lifetimes in, 148
Tetrahydrofuran
pseudorotation and, 312–15
Thermochemical deposition, 91–94
Thioformaldehyde
Coriolis and Fermi interactions of, 34–37
dipole moments of, 51–52
ground state rotational constants of, 33–34
higher excited states of, 47–51
molecular structure of, 32, 37–39, 45–46
perturbations of, 44–45
rotational structure of, 41, 46–47
singlet-triplet interactions of, 54–56
spectroscopy of, 31–56
vibrational frequencies of, 32, 41–44, 47–48
vibronic structure of, 39–40, 46
Thymidine
polarized fluorescence of, 346–47
Thymine
polarized fluorescence of, 346–47
Triatomic molecules
nonrigid bender Hamiltonians and, 69–70
Triazine
intersystem crossing and, 147–48
Trimethylene oxide
pseudorotation and, 310
Triplet states
applied magnetic fields and, 389–90

U

Uracil
polarized fluorescence of, 346–47
polarized transitions of, 339–43

V

Valine
proton affinity of, 196
Vapor pressure
of supercooled water, 607–8
Vibrational randomization
dispersed fluorescence and, 136–40
excited electronic states and, 131–36
measurements of, 140–47
Vibrational relaxation
formaldehyde photochemistry and, 536–37
Vibrational transition lasers, 565–74
Vibration-rotation spectroscopy, 245–68
Vinylamine
proton affinity of, 195
Viscosity
heat conductivity and, 120–21
supercooled water and, 610–11
Viscous flows
simulation of, 116–20
Vitrification
supercooling and, 593–600

W

Wall-Flory theory of elasticity, 371–73
Wave function theory
density functional theory and, 646–48

X

Xenon hexafluoride
pseudorotation and, 322–23
Xylylenes
proton affinity of, 195

Z

Zeeman effect
dimer electric quadrupole moments and, 298